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Pt-Rh/CeO_2-Al_2O_3 for Controlling Emissions from Natural Gas Engines: Three-Way Catalytic Activity at Low Temperatures and Effects of SO_2 Aging

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Abstract The three-way catalytic activity of Pt-Rh/CeO_2-Al_2O_3 was examined at temperatures below 500 °C under conditions simulating gas engine exhaust, and the results were compared with those of O_2-CH_4, NO-O_2-CH_4, and NO-CH_4 model reactions. The catalyst exhibited sufficient three-way catalytic activity, even at 400 °C, in the absence of SO_2. After SO_2 aging, the activity under stoichiometric conditions remarkably decreased. In addition, methane conversion under rich (reducing) conditions severely decreased after SO_2 aging due to the suppression of steam methane reforming by sulfur poisoning.

Keywords Three-way catalyst (TWC) · Natural gas vehicle (NGV) · Platinum · Rhodium · Methane

1 Introduction

Among fossil fuels, natural gas produces the least carbon dioxide per unit of energy and is thus the most favorable in terms of environmental impact [1]. Recent advances in shale gas exploitation have significantly increased the supply of natural gas and stabilized the price of natural gas, increasing its attractiveness as a fuel [2]. Internal combustion engines fuelled by natural gas are widely used in natural gas vehicles (NGV), combined heat and power (CHP) plants, and gas engine-driven heat pump units (GHP). To control emissions from these engines, three-way catalyst systems similar to those used in gasoline-fuelled vehicles are widely applied. However, in contrast to gasoline engine exhaust, which contains a large amount of reactive hydrocarbons such as C_2H_4 and C_3H_6, the main hydrocarbon component in gas engine exhaust is methane [3]. Because methane is the least reactive hydrocarbon, obtaining a high methane conversion at low temperatures is the principal issue in controlling emissions from natural gas engines by three-way catalysts [4–6].

A Pt-Rh/CeO_2-Al_2O_3 catalyst with high Pt loading has been developed as a catalyst that exhibits high durability under the conditions of emission control from gas engines, with a reported long-term durability of more than 30,000 h [7–9]. However, with growing concerns about global warming and concomitant tightening of fuel efficiency regulations, further increases in the efficiencies of gas engines are sought, and efficiency improvement measures such as exhaust gas recirculation (EGR) are being intensively studied. Improvements in fuel efficiency inevitably cause a decrease in the exhaust temperature. This imposes a further challenge for controlling emissions from natural gas engines. The selective catalytic reduction of NO_x with methane (CH_4-SCR) coupled with lean combustion can be an alternative solution and has been studied extensively [10–15]. However, activities of the reported catalysts are not sufficient to obtain NO_x and CH_4 conversions required in practical applications.

A number of studies have examined three-way catalysts for natural gas engines and related reactions. Subramanian and coworkers extensively investigated model reactions (CH_4-NO-CO-H_2-O_2, CH_4-NO-CO-O_2, CH_4-O_2, CH_4-NO, etc.) over 1 % Pd/Al_2O_3 with different feedstream compositions, from reducing to stoichiometric to oxidizing atmospheres [16]. However, the temperature examined in their study was limited to 550 °C, and activity at lower temperatures was not examined. Oh and coworkers investigated methane oxidation over noble metal (Pt, Pd, Rh) catalysts supported on Al_2O_3 and CeO_2/Al_2O_3 with varying oxygen concentrations between 0.2 and 1 % [17, 18]. They observed that methane conversion was maximal at approximately stoichiometric oxygen concentrations and decreased under oxidizing conditions, concluding

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that the decrease in methane conversion under oxidizing conditions was due to strong adsorption of oxygen on the surface of the noble metals comprising the active sites. Burch and Ramli investigated NO reduction by CH_4 over Pt, Pd, and Rh catalysts supported on SiO_2 and Al_2O_3 [19, 20]. They determined that Pt had the highest activity, which was an order of magnitude higher than those of Pd and Rh. It was suggested that the relative activities of the catalysts reflected the ease of reduction of the catalysts. González-Velasco and coworkers investigated three-way catalytic reactions over Pt/Al_2O_3 in the presence of H_2O (10 %) and CO_2 (10 %), which are present in actual engine exhaust [21]. In a comparison of CH_4, C_2H_4, C_3H_6, and C_4H_8 as the hydrocarbon components, they demonstrated that a high hydrocarbon conversion of ca. 100 % was obtained under net oxidizing conditions when hydrocarbons other than CH_4 were used, while CH_4 conversion was very low except under slightly reducing conditions.

In this work, the three-way catalytic activity of a Pt-Rh/CeO_2-Al_2O_3 catalyst that is widely used in natural gas engines was investigated at relatively low temperatures (400–500 °C) under conditions simulating natural gas engine exhaust. The effects of S poisoning, which are expected to be severe at lower temperatures, were also examined.

2 Experimental

2.1 Catalyst Preparation

Commercial γ-Al_2O_3 (4- to 6-mm spheres, Kishida Chemical, Osaka) was crushed and sieved to 1- to 2-mm grains, which were impregnated with Ce (10 wt%) using an aqueous solution of cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$, Mitsuwa Chemicals, Osaka), followed by drying at 120 °C and calcining in air at 700 °C for 6 h to obtain a CeO_2-Al_2O_3 support.

The support was loaded with Pt (2.0 wt%) and Rh (0.2 wt%) by impregnation using $Pt(NO_2)_2(NH_3)_2$ (Kojima Chemicals, Tokyo) and $Rh(NO_3)_3$ (N.E. Chemcat, Tokyo) as precursors. The impregnated solid was dried at 120 °C and calcined in air at 550 °C for 6 h to obtain the Pt-Rh/CeO_2-Al_2O_3 catalyst.

2.2 Catalytic Activity Measurements

Catalytic activity was measured using a fixed-bed flow reactor. The catalyst grains (1.45 g, ca. 1.9 mL) were placed in a quartz tube (inside diameter 14 mm, length 740 mm) and heated with an electric furnace (ARF3-500, Asahi Rika, Chiba, Japan). The temperature of the catalyst bed was measured with a thermocouple inserted into the quartz tube. The reaction gas was prepared by mixing 5000 ppm NO/He, 3 % CH_4/He, 2 % CO, 1.2 % H_2/He, 30 ppm SO_2/He, O_2 (99.97 %, Takachiho Chemical, Tokyo), CO_2 (99.999 %, Takachiho Chemical), and He (99.999 %, Iwatani Industrial Gases, Osaka) gases using mass flow controllers (HM5141B, Hemmi Slide Rule, Tokyo). Water vapor was introduced by passing a portion of the helium through a water saturator. The gas flow rate was 1.675 L/min, which corresponded to a gas hourly space volume (GHSV) of 53,000/h.

The feedstream compositions shown in Table 1 were used in the experiments under simulated gas engine exhaust conditions. The compositions were similar to those of actual gas engine exhaust, except the concentrations of CO_2 and H_2O, which were reduced for experimental accuracy. The O_2-CH_4, NO-O_2-CH_4, and NO-CH_4 reactions were also examined as model reactions for three-way catalytic reactions. All activity measurements were performed under a range of conditions from rich (reducing) conditions to lean (oxidizing). For activity measurements of model reactions, pretreatment with a gas containing 3000 ppm CO, 1800 ppm H_2, and 5 % H_2O in He for 10 min was conducted before measurements at each temperature.

The feedstream composition was maintained constant for 25 min before the effluent gas was analyzed. A pair of chemiluminescence NO_x analyzers (ECL-88A Lite, Anatec Yanaco, Kyoto) was used to measure NO_x concentrations. The NO_x concentration is the sum of the NO and NO_2 concentrations, and the NO_x conversion (X_{NO}) is calculated by the following equation, where the suffixes "in" and "out" indicate the concentrations at the inlet and outlet of the reactor, respectively.

$$X_{NO}(\%) = 100 \times \left\{1 - \left([NO]_{out} + [NO_2]_{out}\right) \Big/ \left([NO]_{in} + [NO_2]_{in}\right)\right\}$$

The concentrations of H_2, CO, CO_2, CH_4, O_2, and N_2O were measured by gas chromatography (GC-2014ATF and GC-8AIT, Shimadzu, Kyoto). Hydrogen was separated using a MS-13X column (16 m); O_2, N_2, and CO were separated using a MS-5A column (2 m); and CO_2 and N_2O were separated using a Gaskuropack 54 (4 m, GL Sciences, Tokyo). The concentration of each component was measured using a

Table 1 Feedstream compositions for activity measurements under conditions simulating gas engine exhaust. Concentrations of other components were maintained constant: CH_4 1500 ppm, CO_2 6 %, H_2O 11 %

λ	NO (ppm)	O_2 (ppm)	CO (ppm)	H_2 (ppm)
0.985	1400	3440	5000	3000
0.990	1600	3650	4200	2520
0.995	1800	3870	3400	2040
0.998	1920	3990	2920	1750
0.999	1960	4040	2760	1660
1.000	2000	4080	2600	1560
1.002	2080	4170	2280	1370
1.005	2200	4300	1800	1080

thermal conductivity detector (TCD). Methane was separated using a Gaskuropack 54 (2 m) and measured with a flame ionization detector (FID). The minimum detectable concentrations for gas chromatography were approximately 40 ppm for O_2, CO, CO_2, and N_2O; 200 ppm for H_2; and 5 ppm for CH_4.

In experiments under simulated exhaust conditions, catalytic activity was measured from 550 to 400 °C in intervals of 25 °C. After measurements at 400 °C, the catalyst was subjected to SO_2 aging by introducing a gas with a composition of 100 ppm NO, 1000 ppm CO, 600 ppm H_2, 3 ppm SO_2, 1500 ppm CH_4, 5 % O_2, 6 % CO_2, and 11 % H_2O balanced with He for 18 h (flow rate 1.675 L/min) while the temperature of the catalyst bed was maintained at 400 °C. The activity of the aged catalyst was measured from 400 to 550 °C in intervals of 25 °C. The catalytic activity in the model reactions was measured at 500 °C followed by 450 and 400 °C for the fresh catalyst and at 400 °C followed by 450 and 500 °C for the SO_2-aged catalyst. During activity measurements after SO_2 aging, 1 ppm SO_2 was added to the feedstream to avoid depoisoning of the catalyst.

To compare conversions under simulated exhaust conditions with those of the model reactions, the conversions were plotted against the air to fuel equivalence ratio (λ), which is widely used as a parameter for controlling internal combustion engines. The air to fuel equivalence ratio (λ) is defined as the ratio of the actual amount of air introduced into the combustion chamber to the amount of air that is required to completely combust the fuel. When the only exhaust hydrocarbon is CH_4, λ is calculated according to the following equation [5], where the concentrations (ppm) of the species are in brackets.

$$\lambda = 1 + \left([O_2] + 0.5[NO] - 0.5[H_2] - 0.5[CO] - 2[CH_4]\right) \Big/ \left(1.91 \times 10^5\right)$$

2.3 Characterization

Specific surface area measurements were obtained with an automatic surface area analyzer (AMS-8000, Ohkura Riken, Tokyo). The adsorption of N_2 was measured at 77 K and P/P_0=0.3, and the Brunauer-Emmett-Teller (BET) surface area was calculated according to the one-point method. Measurements of CO adsorption were conducted using a pulsed-flow adsorption analyzer (R-6015, Ohkura Riken). Samples were pretreated under a H_2 flow at 200 °C for 30 min, and the adsorption of CO was measured at 50 °C.

Powder X-ray diffraction patterns were measured using Cu Kα radiation on an X-ray diffractometer equipped with a graphite monochromator (XRD-6100, Shimadzu). The X-ray tube (PW2233/20, PANalytical) was operated at 40 kV and a current of 40 mA. The patterns were recorded over a 2θ range of 20° to 74° with a step size of 0.02°, a dwell time of 1.2 s, and a rotation speed of 50 rpm.

3 Results

Figure 1 shows the X-ray diffractograms of the support and the catalyst. In the X-ray diffractogram of the support, diffraction lines for CeO_2 at 28.6°, 33.1°, 47.5°, and 56.3° and for Al_2O_3 at ca. 67° were observed. No appreciable changes in these diffraction lines were observed after loading Pt-Rh or after activity measurements. Table 2 shows the BET specific surface areas and CO adsorption results. The changes in the BET surface areas were also small. These results suggest that the support itself was not essentially affected by the loading of Pt-Rh or the activity measurements. In the X-ray diffractogram of the catalyst, a broad diffraction line for metallic Pt was observed at ca. 40°. The intensity of this line increased after activity measurements, suggesting that the supported Pt agglomerated to form metallic Pt particles under the reaction conditions. A significant decrease in the amount of CO adsorbed was observed after activity measurements. The catalysts exhibited a larger decrease in the amount of CO adsorbed after SO_2 aging, which may indicate that sulfur promoted Pt agglomeration, but the adsorbed sulfur species that remained after pretreatment may have inhibited the adsorption of CO, reducing the amount of CO adsorption on the SO_2-aged catalysts.

Figure 2 shows the NO_x, CO, and CH_4 conversions under conditions simulating gas engine exhaust. Over the fresh (before SO_2 aging) catalyst at 550 °C, all of the NO_x, CO, and CH_4 conversions exceeded 99 % under stoichiometric conditions (λ=1.000). Under rich conditions (λ<1.000), CO conversion decreased, but high CH_4 conversion was maintained. By contrast, under lean conditions (λ>1.000), NO_x conversion sharply decreased, with an increase in λ accompanied by a slight decrease in CH_4 conversion. As the reaction temperature decreased, the NO_x and CH_4 conversions

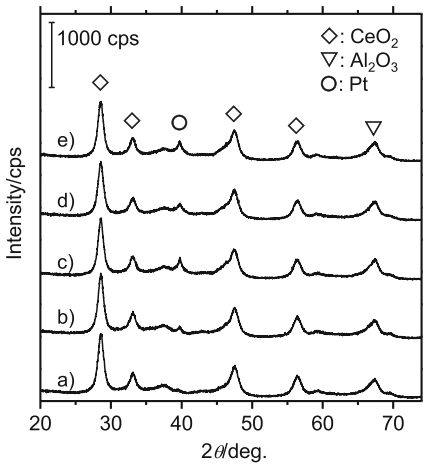

Fig. 1 X-ray diffractogram of the support and catalyst. *a)* CeO_2-Al_2O_3, *b)* Pt-Rh/CeO_2-Al_2O_3, *c)* Pt-Rh/CeO_2-Al_2O_3 after reaction under simulated gas engine exhaust conditions, *d)* Pt-Rh/CeO_2-Al_2O_3 after reaction under model gas conditions without S aging, and *e)* Pt-Rh/CeO_2-Al_2O_3 after reaction under model gas conditions with S aging

Table 2 BET surface areas and amounts of CO adsorption on the support and catalysts

	BET surface area (m^2/g)	CO adsorption (mL/g)
CeO_2-Al_2O_3	109	–[a]
Pt-Rh/CeO_2-Al_2O_3		
As prepared	106	1.09
After activity measurements		
Under simulated exhaust	102	0.242
Under model reactions without S aging	105	0.466
Under model reactions with S aging	105	0.281

[a] Not measured

decreased under stoichiometric conditions (λ=1.000), with NO_x and CH_4 conversions at 400 °C of 91 and 89 %, respectively. CH_4 conversion under lean conditions decreased remarkably at lower temperatures, and CH_4 conversion also decreased under rich conditions. Concomitant with the decrease in CH_4 conversion under rich conditions, the CO conversion under rich conditions increased. That is, when components in the effluent gas were compared at the same λ, the concentration of CH_4 increased and the concentrations of CO and H_2 decreased. At all temperatures between 400 and 550 °C, the reaction effluent contained H_2 at a concentration of 4000–6000 ppm at λ=0.985, higher than the H_2 concentration in the feedstream. These results suggest that H_2 was formed by steam reforming of CH_4. The concentration ratio of H_2/CO was 5.9 (550 °C)–17 (400 °C), which is nearly identical to the ratio in the chemical equilibrium of the water-gas shift reaction (6.1 [550 °C]–21 [400 °C]). The effect of SO_2 aging on NO_x and CH_4 conversion was remarkable at 500 °C and lower temperatures under stoichiometric conditions (λ=1.000). After SO_2 aging, NO_x and CH_4 conversions decreased to 72 and 70 %, respectively, at 400 °C. While the CH_4 conversion under rich conditions remarkably decreased after SO_2 aging, the CH_4 conversion under lean conditions was affected very little or slightly increased. The effluent from the aged catalyst under rich conditions contained almost solely CH_4 as the reducing component, while the concentrations of H_2 and CO were very low or below the detection limits. The conversion of CH_4 at λ=0.985–0.995 did not change appreciably with the reaction temperature, most likely because CH_4 conversion was determined by the feedstream composition and not the reaction rate. In fact, under conditions of λ=0.985–0.995, the NO_x and O_2 conversions were ca. 100 % between 400 and 550 °C, and the observed CH_4 conversion corresponded to the calculated CH_4 conversion under the assumption that excess reducing components exit the reactor as methane (5, 36, and 68 % for λ=0.985, 0.990, and 0.995, respectively).

Figure 3 shows the N_2 yield from the activity measurements shown in Fig. 2. Over the fresh catalyst, the N_2 yield was in good agreement with the NO conversion under stoichiometric to lean conditions, which indicates that NO was converted to N_2 with high selectivity. By contrast, under rich conditions, the N_2 yield decreased significantly with decreasing λ. Under the experimental conditions, the large amount of CO_2 contained in the feedstream prevented precise determination of the effluent N_2O concentration, but formation of a large amount of N_2O can be ruled out. Therefore, NO that was not converted to N_2 most likely formed NH_3. After SO_2 aging, a decrease in the N_2 yield under rich conditions was not observed, and at 450 °C or higher, the N_2 yield was in good agreement with the NO conversion throughout the entire λ range examined. As mentioned above, the reaction effluent contained large amounts of H_2 before SO_2 aging but only small amounts of H_2 after SO_2 aging. Large amounts of NH_3 are formed in the NO-H_2 reaction over Pt catalysts under H_2-rich conditions [22]; the suppression of the formation of H_2, which is required to form NH_3, is likely responsible for the suppression of NH_3 formation after SO_2 aging.

Figure 4 shows the CH_4 conversion in the activity measurements under the simulated exhaust conditions as a function of temperature. Over the fresh catalyst, the CH_4 conversion at λ=0.985 was 82 % at 400 °C and increased with increasing reaction temperature, reaching 98 % at 500 °C.

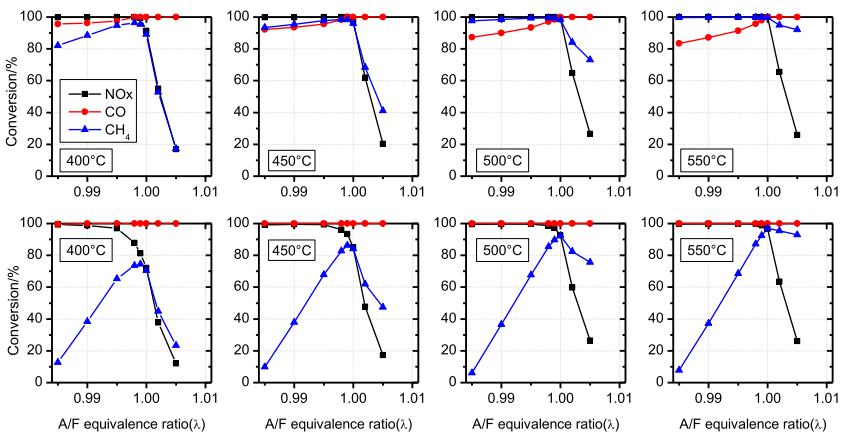

Fig. 2 NO_x, CO, and CH_4 conversions over Pt-Rh/CeO_2-Al_2O_3 under gas engine exhaust conditions before (*upper column*) and after (*lower column*) S aging

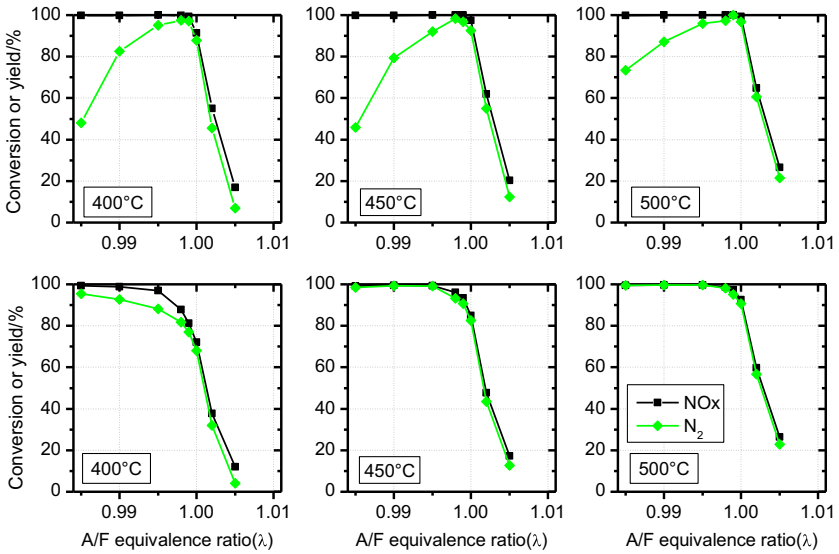

Fig. 3 NO_x conversions and N_2 yields over Pt-Rh/CeO_2-Al_2O_3 under gas engine exhaust conditions before (*upper column*) and after (*lower column*) S aging

Under lean conditions (λ=1.005), the CH_4 conversion was 17 % at 400 °C, considerably lower than that under rich conditions. CH_4 conversion under lean conditions also increased with increasing reaction temperature but reached only 73 % at 500 °C and 92 % at 550 °C. The effects of SO_2 aging on CH_4 conversion were remarkably different under rich or lean conditions. Under lean conditions, SO_2 aging did not affect or slightly promoted CH_4 conversion. By contrast, SO_2 aging drastically suppressed CH_4 conversion under rich conditions. CH_4 conversion after SO_2 aging exhibited a maximum at 425 °C and decreased with increasing temperature up to 500 °C.

Figure 5 shows the CH_4 conversion in the O_2-CH_4 reaction. Before SO_2 aging, a high CH_4 conversion was observed under stoichiometric and rich conditions. At λ=1.000, the CH_4 conversion was 91 % at 400 °C and ca. 100 % at 500 °C. At λ=0.984, the CH_4 conversion was 84 % at 400 °C and ca. 100 % at 500 °C. By contrast, under lean conditions, the CH_4 conversion decreased with increasing λ. At 400 °C, the CH_4 conversion fell to 16 % at λ=1.010. The feedstream composition at λ=0.984 was 1500 ppm CH_4 and 11 % H_2O balanced with He. Obviously, the CH_4 was converted solely by steam reforming under this condition, as demonstrated by H_2 formation. The reaction

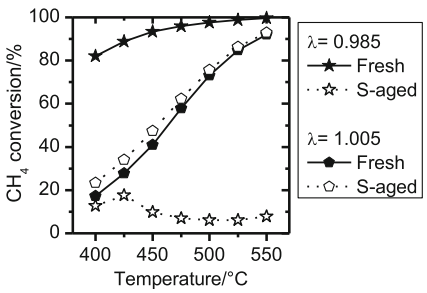

Fig. 4 CH_4 conversions over Pt-Rh/CeO_2-Al_2O_3 as a function of temperature under gas engine exhaust conditions

effluent contained ca. 6000 ppm H_2 at 500 °C and ca. 5000 ppm H_2 at 400 °C, in agreement with the calculated H_2 concentrations assuming steam reforming and water-gas shift reactions (H_2 4 mol/mol-CH_4). In the presence of O_2, the concentration of H_2 decreased, but H_2 formation was still observed (ca. 2000 ppm H_2 at 500 °C and λ=0.995, i.e., CH_4 1500 ppm, O_2 2000 ppm, 11 % H_2O).

The effects of SO_2 aging on CH_4 conversion in the O_2-CH_4 reaction differed substantially under rich or lean conditions. Under rich conditions, CH_4 conversion was drastically suppressed, and H_2 formation became insignificant after SO_2 aging, indicating nearly complete suppression of steam reforming of CH_4. By contrast, SO_2 aging did not significantly affect CH_4 conversion under lean conditions. The CH_4 conversion characteristics and the effects of SO_2 aging in the O_2-CH_4 reaction resembled those under simulated exhaust conditions.

Figure 6 shows the NO_x and CH_4 conversions in the NO-O_2-CH_4 reaction. Over the fresh catalyst, a NO_x conversion of 93 % and a CH_4 conversion of 93 % were obtained under stoichiometric conditions (2000 ppm NO, 2000 ppm O_2, 1500 ppm CH_4) at 400 °C, in good agreement with the NO_x and CH_4 conversions under simulated exhaust conditions (91 and 89 %, respectively). After SO_2 aging, the NO_x and CH_4 conversions in the NO-O_2-CH_4 reaction were also similar to those under simulated exhaust conditions.

Figure 7 shows the N_2 and N_2O yields in the NO-O_2-CH_4 reaction. Over the fresh catalyst, the N_2 yield was in good agreement with the NO_x conversion under stoichiometric to lean conditions but decreased with decreasing λ under rich conditions. Because N_2O was not observed in the effluent under rich conditions, the NO_x that did not form N_2 was likely converted to NH_3. After SO_2 aging, N_2O formation was observed at 400 °C, λ=0.995 (N_2O yield 7 %), but the N_2

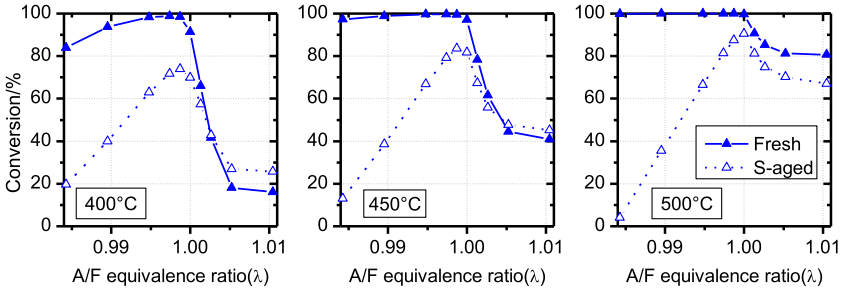

Fig. 5 CH_4 conversions over Pt-Rh/CeO_2-Al_2O_3 in the O_2-CH_4 reaction. Reaction conditions: 1500 ppm CH_4, 0–5000 ppm O_2, 11 % H_2O

yield was otherwise nearly in agreement with the NO_x conversion. Similar to the results obtained under simulated exhaust conditions, the effluent from the fresh catalyst contained H_2 under rich conditions, with a H_2 concentration of ca. 2000 ppm at λ=0.995. These results indicate that the NO_x and CH_4 conversions and the N_2 yield in the NO-O_2-CH_4 reaction are in good agreement with those obtained under simulated exhaust conditions.

Figure 8 shows the NO_x and CH_4 conversions in the NO-CH_4 reaction. At 400 °C, λ=1.000, the NO_x conversion was 99.7 % over the fresh catalyst and 96 % over the SO_2-aged catalyst. At 450 and 500 °C, the NO_x conversion at λ=1.000 was ca. 100 % over both of the fresh catalyst and the SO_2-aged catalyst. These conversions are remarkably higher than those observed under simulated exhaust conditions or in the NO-O_2-CH_4 reaction. However, the NO_x and CH_4 conversions decreased under lean conditions. Under rich conditions, H_2 formation was observed over the fresh catalyst but not the SO_2-aged catalyst, which indicates that the fresh catalyst efficiently catalyzed steam reforming of CH_4 but was suppressed by sulfur poisoning. In these respects, the results of the NO-CH_4 reaction resemble those obtained under simulated exhaust conditions or in the NO-O_2-CH_4 reaction.

Figure 9 shows the N_2 yield from the NO-CH_4 reaction. Regardless of the reaction temperature and SO_2 aging, a high N_2 yield was obtained under stoichiometric conditions, but significant N_2O formation was observed under lean conditions. N_2O formation was observed at 400 and 450 °C after SO_2 aging. In particular, at 400 °C and λ=0.990, a large discrepancy was observed between the NO_x conversion and the N_2+N_2O yield, suggesting that a significant amount of NH_3 was formed.

4 Discussion

Many reactions proceed simultaneously over three-way catalysts under conditions of actual emission control, and the chemistry of three-way catalysis is complicated [23]. When methane is the only the hydrocarbon species in the feedstream, as was investigated in this study, and only N_2 is considered as a product of NO_x reduction, the following reactions contribute to exhaust purification:

$$H_2 + NO \rightarrow 1/2\ N_2 + H_2O \quad (1)$$

$$CO + NO \rightarrow 1/2 N_2 + CO_2 \quad (2)$$

$$H_2 + 1/2\ O_2 \rightarrow H_2O \quad (3)$$

$$CO + 1/2\ O_2 \rightarrow CO_2 \quad (4)$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (5)$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2H_2O \quad (6)$$

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O \quad (7)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (8)$$

Among these reactions, the reaction of NO (or O_2) and CO (or H_2) proceeds rapidly at temperatures of 300 °C or higher over noble metal catalysts. For example, Kobykinski and Taylor reported that NO reduction by H_2 over 0.5 wt% Pt/Al_2O_3 gave 50 % conversion of NO at 121 °C and that NO

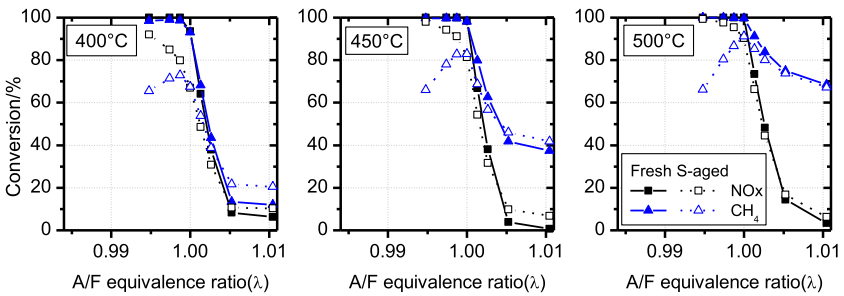

Fig. 6 NO_x and CH_4 conversions over Pt-Rh/CeO_2-Al_2O_3 in the NO-O_2-CH_4 reaction. Reaction conditions: 2000 ppm NO, 1500 ppm CH_4, 1000–4000 ppm O_2, 11 % H_2O

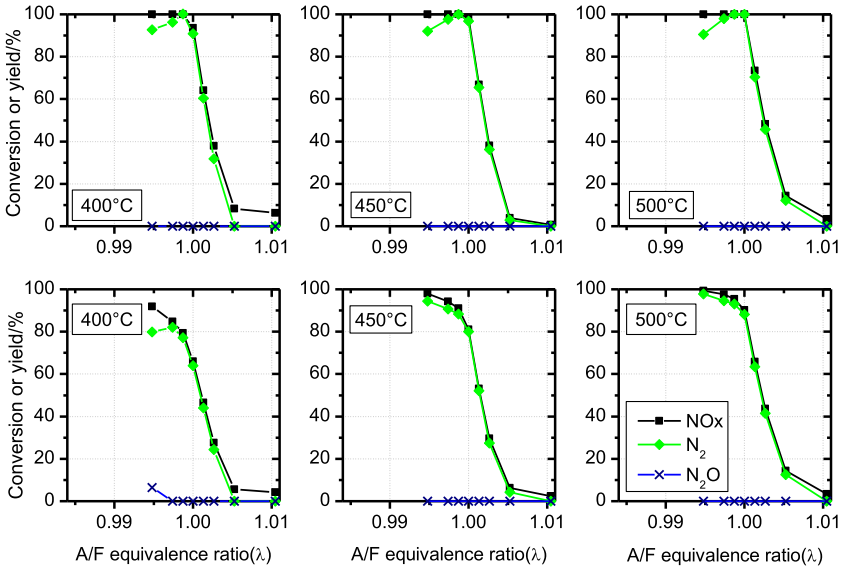

Fig. 7 NO_x conversions and N_2 and N_2O yields over Pt-Rh/CeO_2-Al_2O_3 in the NO-O_2-CH_4 reaction before (*upper column*) and after (*lower column*) S aging. The reaction conditions were the same as in Fig. 6

reduction by CO over 0.5 wt% Rh/Al_2O_3 gave 50 % conversion of NO at 296 °C [24]. Oh and coworkers investigated the CO-CH_4-O_2 reaction over 0.2 wt% Pt/Al_2O_3 and 0.14 wt% Rh/Al_2O_3 catalysts. They observed complete conversion of CO at 200 °C over Pt/Al_2O_3 and at 400 °C over Rh/Al_2O_3 in an oxidizing feedstream and at 200 °C over both of Pt/Al_2O_3 and Rh/Al_2O_3 in a reducing feedstream [17]. By contrast, reactions involving CH_4 (reactions 6–8) proceed relatively slowly under the conditions used in this study (400–550 °C).

Steam reforming of CH_4 (8) is a highly endothermic reaction ($\Delta H°$=206 kJ/mol) and is controlled by a thermodynamic equilibrium under typical conditions for H_2 production from CH_4. However, under the conditions examined in this study (1500 ppm CH_4, 11 % H_2O, 6 % CO_2, 400–550 °C), the equilibrium conversions of CH_4 are 99 % or higher, that is, the reaction is controlled by the reaction rate rather than the chemical equilibrium. The water-gas shift reaction (5) is a slightly exothermic reaction ($\Delta H°$=−41 kJ/mol) and is controlled by a chemical equilibrium with H_2/CO ratios of ca. 6–20 under the conditions in this study (11 % H_2O, 6 % CO_2, 400–550 °C).

Therefore, in the three-way catalytic reaction under the conditions of gas engine exhaust at low temperatures, reactions of NO (or O_2) and CO (or H_2) are completed in an upstream part of the catalyst bed, and the overall conversion is determined by reactions involving CH_4 (i.e., reactions 6–8) and the equilibrium-controlled water-gas shift reaction (5). Accordingly, the NO_x and CH_4 conversions under simulated exhaust conditions were in good agreement with those in the NO-O_2-CH_4 reaction.

The methane conversion characteristics under the simulated exhaust conditions and in the NO-O_2-CH_4 reaction were in good agreement with those in the O_2-CH_4 reaction, and a large decrease with increasing λ under lean (λ>1) conditions was observed for all reactions. It is widely accepted that the CH_4 oxidation activities of Pt and Rh catalysts are maximal at approximately stoichiometric conditions and decrease under lean conditions due to strong adsorption of oxygen onto the active sites [17, 18].

The effects of SO_2 aging were small under lean conditions, but the NO_x and CH_4 conversions under stoichiometric conditions decreased remarkably at 450 °C and lower temperatures, while CH_4 conversion decreased drastically under rich conditions. Ansell and coworkers investigated the effects of SO_2 aging on the three-way catalytic reactions over Pt-Rh/CeO_2-Al_2O_3 in simulated exhaust containing CH_4 and C_3H_8 [25]. They reported that CH_4 conversion under a lean condition of λ=1.02 slightly increased after SO_2 aging, while CH_4 conversion under a rich condition of λ=0.98 remarkably decreased after SO_2 aging. They concluded that the large

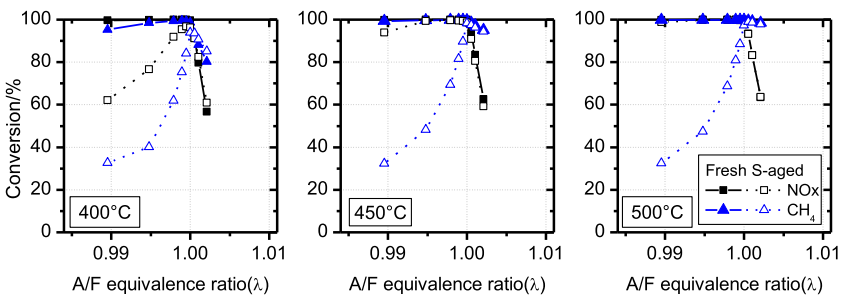

Fig. 8 NO_x and CH_4 conversions over Pt-Rh/CeO_2-Al_2O_3 in the NO-CH_4 reaction. Reaction conditions: 2000 ppm NO, 300–1500 ppm CH_4, 11 % H_2O

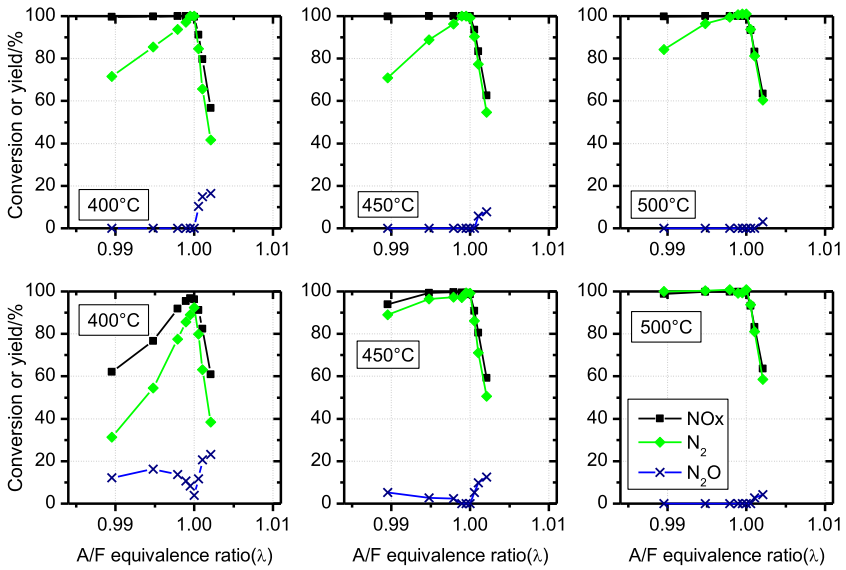

Fig. 9 NO_x conversions and N_2 and N_2O yields over Pt-Rh/CeO_2-Al_2O_3 in the NO-CH_4 reaction before (*upper column*) and after (*lower column*) S aging. The reaction conditions were the same as in Fig. 8

decrease in CH_4 conversion was caused by suppression of steam reforming due to sulfur poisoning. They also reported that the CH_4 conversion of the SO_2-aged catalyst under rich conditions was maximal at 425 °C and decreased with increasing temperature up to 550 °C, in agreement with the results of the present study shown in Fig. 3. Taken together with the decrease in CH_4 conversion in the NO-O_2-CH_4 reaction and the reaction under simulated exhaust as well as in the O_2-CH_4 reaction, these results indicate that the decrease was caused by the suppression of steam reforming. The decrease in NO_x and CH_4 conversions under stoichiometric conditions after SO_2 aging may be explained as follows. Over the fresh catalyst, in addition to the reaction path in which CH_4 reacts directly with O_2 and NO, another path exists in which CH_4 is converted to H_2 and CO via steam reforming, and the subsequent H_2 and CO react with O_2 and NO. Because the latter path is inhibited by sulfur poisoning, the reaction of CH_4 is limited to direct reactions with O_2 and NO, which leads to decreased activity.

By contrast, the NO_x and CH_4 conversions under the simulated exhaust conditions and in the NO-O_2-CH_4 reaction were strongly affected by SO_2 aging and were not sufficient at 450 °C or lower temperatures, and NO_x and CH_4 conversions in the NO-CH_4 reaction at approximately stoichiometric conditions remained high even after SO_2 aging. The NO-CH_4 reaction over Pt/Al_2O_3 has been investigated by Burch and Ramli [19, 20] and by Balint and coworkers [26], but these reports mainly focused on experiments under rich conditions, and catalytic activity under stoichiometric conditions and the differences between the NO-CH_4 and the NO-O_2-CH_4 reactions remained unclear. The high NO_x and CH_4 conversion in the NO-CH_4 reaction under stoichiometric conditions observed in the present study may be explained as follows. Under stoichiometric conditions in the NO-O_2-CH_4 reaction, O_2, which is present at high concentrations, strongly adsorbs onto active sites and prevents the reaction of CH_4 and NO. In the NO-CH_4 reaction, the absence of O_2 increases the number of active sites available for reaction. If it is possible to increase activity by removing O_2 in the reactant, a combination of oxygen storage materials (e.g., CeO_2) and suitable control of the air/fuel ratio may be effective for improving activity at lower temperatures. This effect may partly contribute to improved activity under periodic air/fuel control actually applied to automotive emission control systems [27–29]. However, an insignificant amount of N_2O, which has a high global warming potential, was formed in the NO-CH_4 reaction at low temperatures under both rich and lean conditions. Suppression of N_2O formation would be required to implement this strategy for improving low-temperature activity in practical applications.

5 Conclusions

This work demonstrates that Pt-Rh/CeO_2-Al_2O_3 exhibits sufficient three-way catalytic activity for controlling emissions from natural gas engines, even at 400 °C, in the absence of SO_2. However, the catalyst is sensitive to sulfur poisoning, and its activity is insufficient at temperatures of 450 °C or lower. The decrease in activity is mainly due to suppression of steam reforming of CH_4. Next-generation natural gas engines will have improved efficiencies, and the exhaust temperatures of these improved engines will be lower than those of current engines. Therefore, further catalyst improvements will be required to ensure low emissions from these improved engines, and the key issue will be to promote CH_4 conversion at low temperatures even in the presence of SO_2.

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